"Synthetic Utility of Ionic Liquids for Development of Greener Alternatives in Organic Synthesis"

The Synopsis submitted
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For the Degree of
Doctor of Philosophy (Ph. D.)
In the subject
Chemistry
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Science and Technology

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Introduction

Ionic liquids (ILs) are a promising group of solvents that have special properties that make them appealing for a variety of applications[1]. Ionic liquids are made up of ions, which makes them non-volatile, have low vapor pressure and high thermal stability, and are tunable in physical and chemical properties[2]. They are versatile solvents that can be used in a variety of chemical reactions and separations, as well as in material syntheses[3][4].

In recent years, green chemistry has become increasingly important due to the growing concern about the environmental effects of chemical processes[5][6]. Organic solvents like chloroform (Chloro), benzene (Dichloromethane) and other organic solvents are widely used in chemical reactions but can be hazardous to health and the environment[7]. They are flammable, volatile, toxic and have been linked to air pollution, water pollution and other negative health effects[8]. Finding greener alternatives to organic solvents is essential for sustainable development [9][10].

Ionic liquids offer several advantages over traditional organic catalysts and solvents, making them attractive for green chemistry applications[11][12]. First, their non-volatility and low vapor pressure reduce the release of volatile organic compounds (VOCs) into the atmosphere, minimizing air pollution and improving the safety of chemical processes. Second, their high thermal stability allows for the use of elevated temperatures without the risk of solvent decomposition, enabling faster and more efficient reactions[13]. Third, their high solvation power and unique solvation properties make them effective solvents for a wide range of chemical reactions, including those that are challenging or impossible to perform using traditional solvents [14][15].

The tunable nature of ILs allows for the design and synthesis of solvents with specific properties tailored to a particular application[16][17]. The cation and anion components of an IL can be chosen to optimize its properties, such as polarity, viscosity, hydrophobicity, and acidity/basicity[18]. This ability to fine-tune the solvent properties enables ILs to be tailored for specific chemical reactions, facilitating the development of more efficient and selective processes. Additionally, ILs can be functionalized by incorporating specific functional groups into their structure, further expanding their synthetic utility [19][20].

ILs have been successfully employed in various chemical reactions, including organic synthesis, catalysis, extraction, and electrochemistry[21][22].Their unique properties have been exploited to enhance reaction rates, selectivity, and yields, leading to more sustainable and efficient processes[23]. For example, ILs have been used as reaction media for the synthesis of pharmaceuticals, polymers, and fine chemicals, demonstrating improved yields and reduced waste generation compared to traditional solvents. In catalysis, ILs have been utilized as solvents, co-solvents, or catalyst immobilization media, allowing for enhanced catalyst stability and recyclability[24].

Moreover, ILs have shown potential in extraction processes, where they can replace volatile and toxic organic solvents, reducing environmental hazards and improving product purity[25].

The development of greener alternatives to traditional solvents requires a thorough understanding of the properties and behavior of ILs[26].
Despite their numerous advantages, Is also present challenges and limitations that must be addressed for their widespread adoption[27]. For instance, ILs can have high viscosities, which may hinder mass transfer and reaction kinetics. Furthermore, their high costs and potential toxicity raise concerns about their scalability and environmental impact. Therefore, extensive research is still needed to optimize IL properties, develop efficient synthesis methods, and evaluate their environmental and health effects[28].

Ionic liquids have emerged as promising solvents for the development of greener alternatives in various chemical processes[29]. Their unique properties, including non-volatility, low vapor pressure, high thermal stability, and tunability, make them attractive for applications in organic synthesis, catalysis, extraction, and electrochemistry[30]. By replacing traditional organic solvents, ILs can contribute to the reduction of air and water pollution, minimize health risks, and improve the sustainability of chemical processes. However, further research is needed to address challenges associated with their high viscosity, cost, and potential toxicity[31].

The synthesis and application of ILs should be conducted with careful consideration of their environmental and health impacts[32].

Purpose and objectives of the study.

The purpose of the study on the synthetic utility of ionic liquids for the development of greener alternatives in organic synthesis is to explore the potential of using ionic liquids as sustainable and environmentally friendly options in some chemical processes.

The objectives of the study are:

To achieve the above mentioned aim, the objectives of the research work are prescribed as:

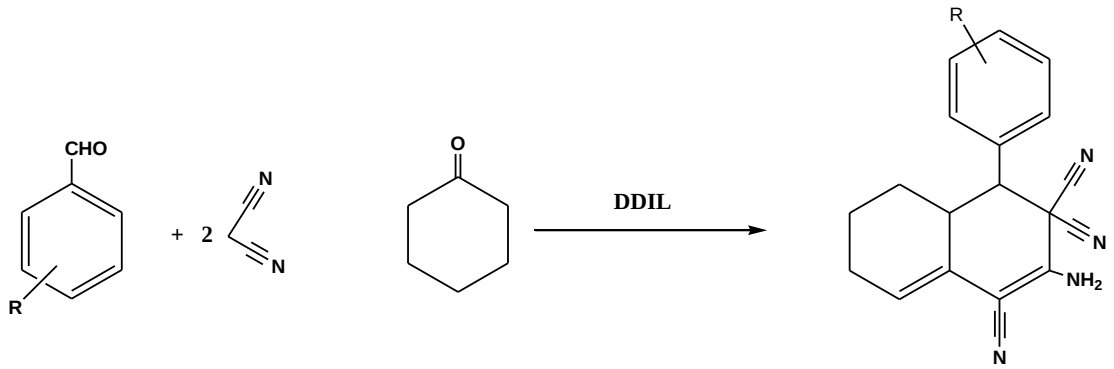
1.To investigating the unique properties and characteristics of ionic liquids that make them suitable for greener alternatives.
2.To evaluating the potential of ILs as sustainable solvents or catalysts in some chemical reactions.
3.To charactrized synthesized compound by using IR,NMR,mass spectroscopy and further instrumentation.
4.To investigating the impact of ILs on reaction rates, selectivity, and overall process efficiency compared to conventional solvents.
5. To providing recommendations for the wider adoption and implementation of ionic liquids as sustainable alternatives in chemical synthesis.

Review of literature survey:

1- Khushboo Verma et al. (2021) , reported dicationic ionic liquids as effective catalysts in solvent freestrecker synthesis, a benign protocol for the Strecker synthesis of α-aminonitriles in the bifunctional ionic liquids[33].

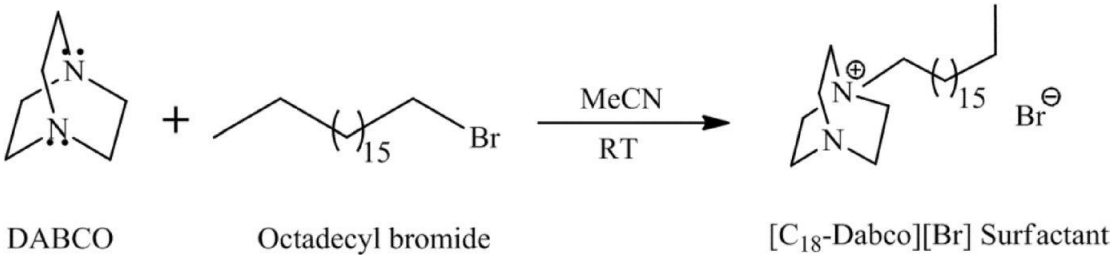
2- Priya A. Thomas et al .2016 ,reported Room Temperature Ionic Liquids as Green Solvent Alternatives in the Metathesis of Oleochemical Feedstocks,as One of the most important areas of green chemistry is the application of environmentally friendly solvents in catalysis and synthesisdue to their ease of reuse, non-volatility, thermal stability and ability to dissolve a variety of organic and organometallic compounds[34].

3- Trushant Lohar et al.2016 reported DABCO functionalized dicationic ionic liquid (DDIL): A novel green benchmark in multicomponent synthesis of heterocyclic scaffolds under sustainable reaction conditions.for development of an alternate mild and cleaner procedure, for the synthesis of *ortho*-amino carbonitriles[35].

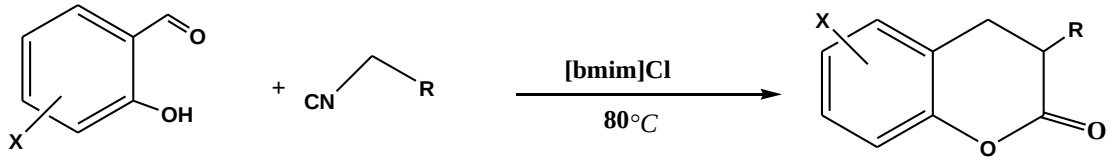


R : Cl,Br,F,OH,CH_3,

4- Trushant Lohar et al. 2019, reported Synthesis and characterization of new quaternary ammonium surfactant [C18‑Dabco][Br] and its catalytic application in the synthesis of spirocarbocycles under ultrasonic condition, A novel DABCO-based cationic surfactant [C18-Dabco][Br] has been easily synthesized by the reaction of DABCO and octadecyl bromide in acetonitrile at room temperature in excellent yield[36].



5- Rahul K. Jadhav et al .2022, reported [Bmim]Cl Mediated Synthesis of Novel 3-(pyridine-2-yl)/Phenyl-2H-Chromene-2-one Derivatives Under Solvent-Free Conditions and their ,Antibacterial, Antifungal Antioxidant Study [37].



X = F, Br, m-tolyl, CH3

R = Pyridine, 4-F phenyl, 4-CF3 Phenyl

Features of Ionic liquids:

1.They are non-volatile at elevated temperatures
2.They are immiscible with water, saturated hydrocarbons dialkyl ethers and a numbers of common organic solvents.
3. Many Ionic liquids liquids are highly polar and non-coordinating ideas for catalytic reactions.
4.They provide flexibility for reaction and separation schemes
Since both the thermodynamic and kinetics of reactions carried out in ionic liquids are different from those in conventional media, they offer new opportunities foe catalytic reactions, separations, electrochemistry.

Importance of Ionic liquid:

As constraints of environment are becoming more and more stringent, organic reactions, catalytic processes and separation technologies require the development of alternative solvents and technologies. The ideal solvent should have a very low volatility, it should be chemically and physically stable, recyclable and reusable and eventually easy to handle. In addition solvents that allows more selective and rapid transformations will have a significant impact.
Room temperature ionic liquids, especially those based on 1-alkyl-3-methylimidazolium cations, have shown great promise as an attractive alternative to conventional organic solvents and more intention has been currently focused on organic reactions promoted by ionic liquids. They are non-volatile, recyclable, non-explosive and thermally robust.

Proposed Plan:

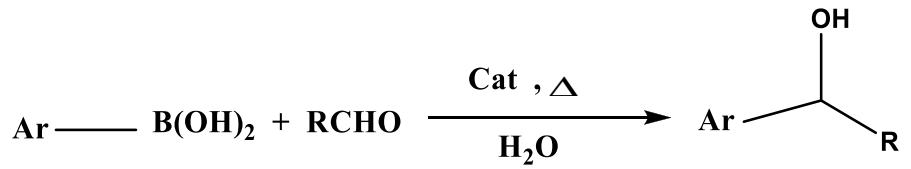
1. Literature survey.
2. Study of ionic liquids as an efficient promoting medium for organic synthesis.
a) Study of ionic liquids as an green solvent.
b) Study of ionic liquids as an efficient promoter for organic synthesis.
c) Development of new methods of organic synthesis using ionic liquids.
d) Study of multicomponent reactions using ionic liquids.
3. Characterization of products using IR., NMR. Mass Spectroscopy and further instrument.
4. Publishing the results in journals of National/ International repute.
5. Submission of thesis.

Research design and methodology:

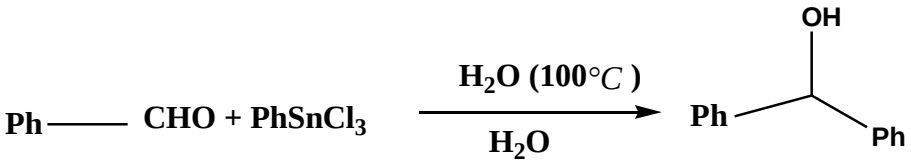
MILE STONE I

A) Use of water as a green solvent in organic synthesis:

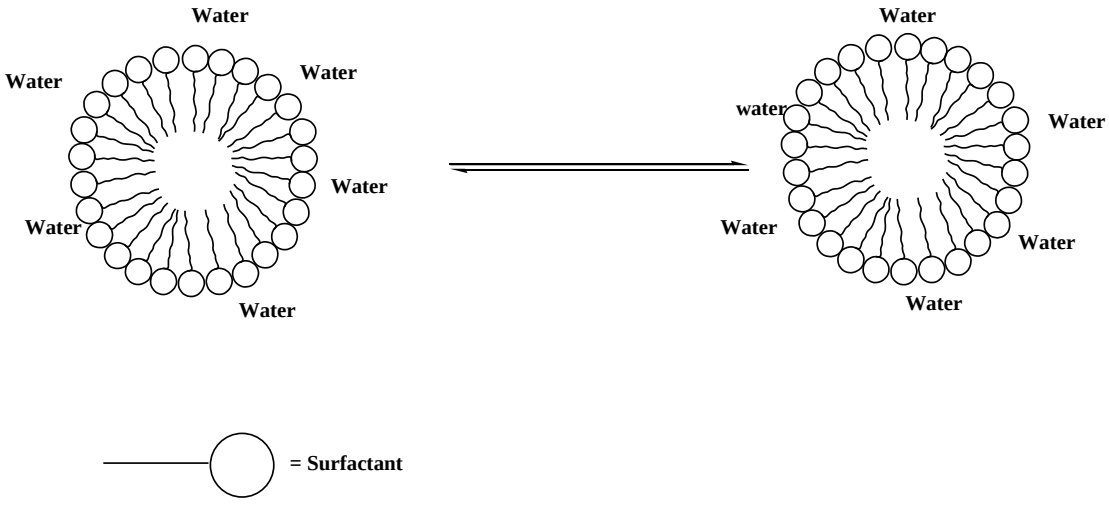
1) Addition of boranic acid derivatives to aldehydes in an aqueous Condition:



2) Phenylation in water:

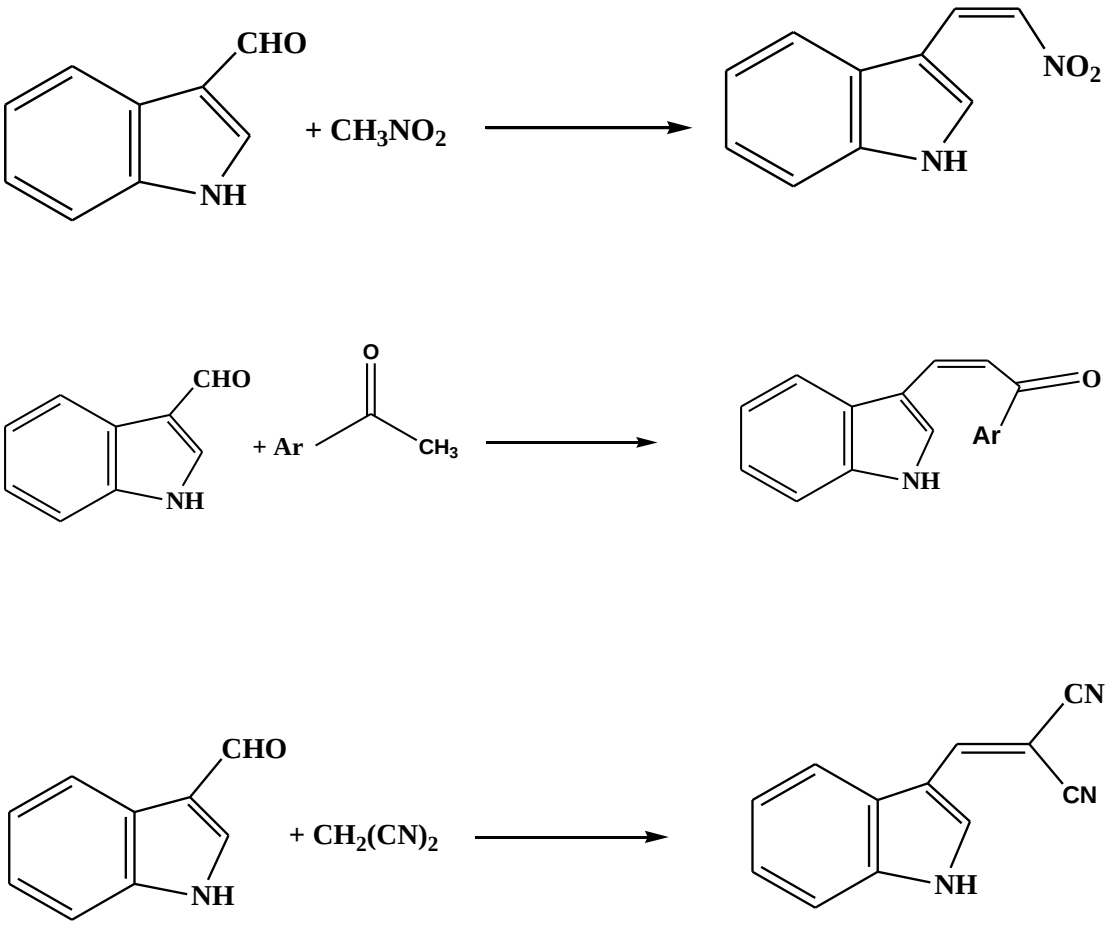


B) Dehydration in water using surfactant type catalyst:

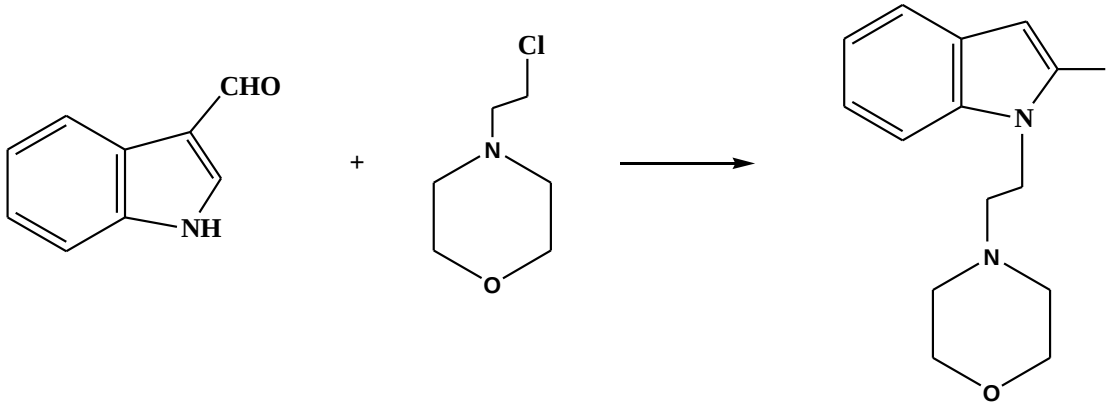


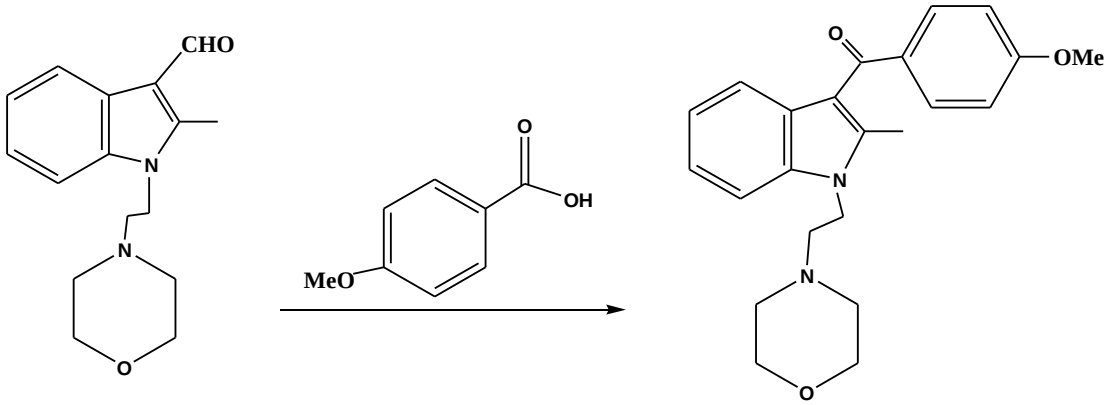
Mile Stone II

A) Solvent free synthesis of Indole derivatives:



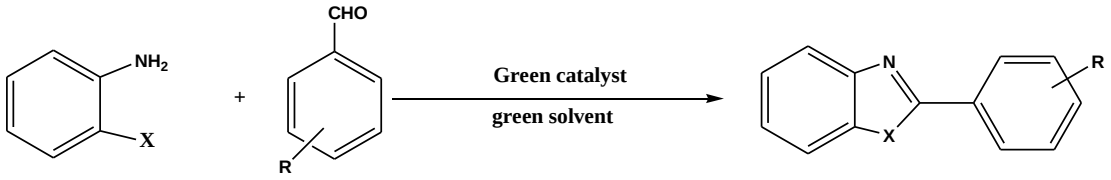
B) Total synthesis of Pharmaceutical Pyaradoline:





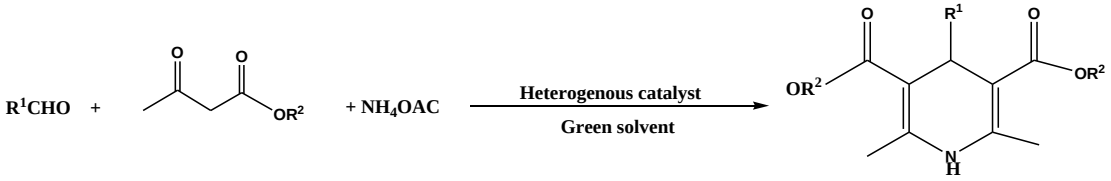
Mile Stone III

A) 1) Syathesis of Benzodiazole, Benzothiazole and Benzoxazole:



X= NH_2 , SH , OH

2) Synthesis of Biginelli Compounds:



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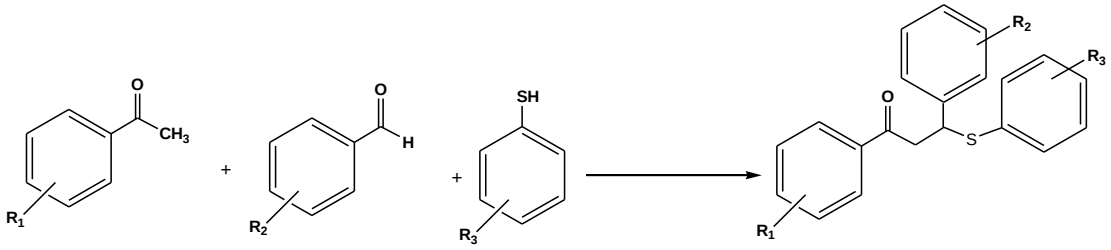
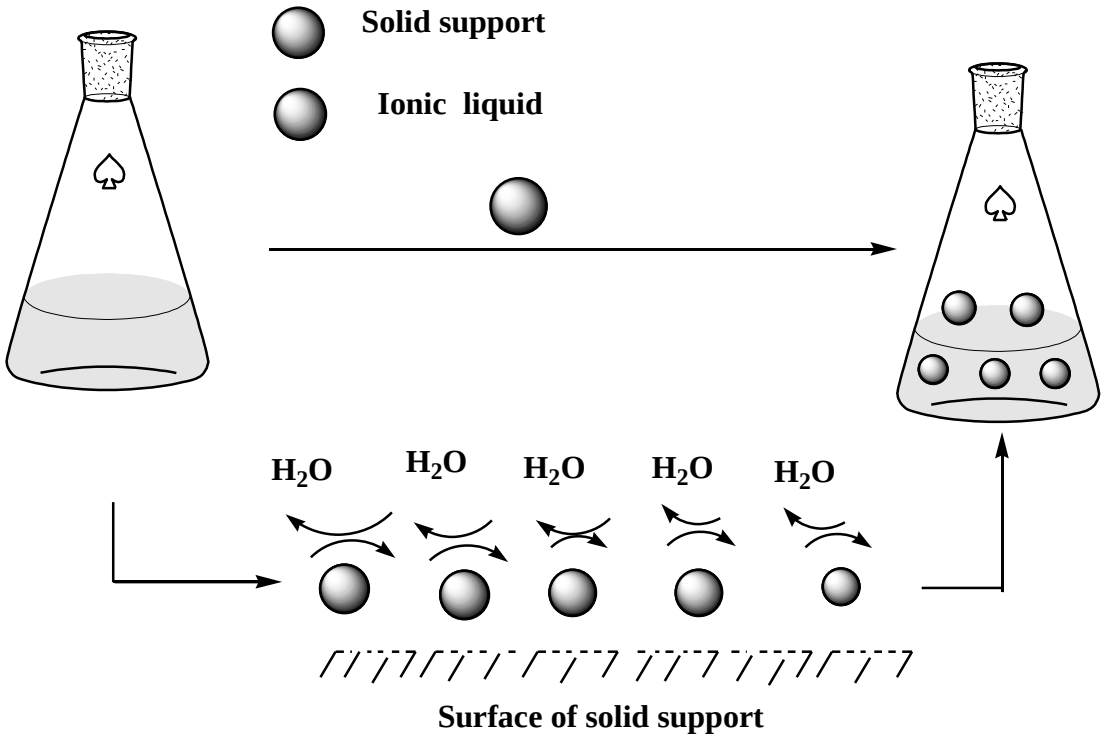


B) Study of organic reaction using solid support-water system:

An alternative aqueous/co-solvent solid supported catalyst will be prepared by using a coating of Ionic liquid and will be applied for organic synthesis.



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